California Environmental Protection Agency

Air Resources Board

DRAFT

SOURCE TEST PROTOCOL

Select Hazardous Air Pollutant Emissions From Phase II Vapor Recovery Combustion Processors

MONITORING AND LABORATORY DIVISION
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Phase II Vapor Recovery Combustion Processors

I.0 INTRODUCTION

1.1 Objectives

The objectives of this test are to determine volume flow and emissions of carbon monoxide (CO), oxides of nitrogen (NOx), and selected hazardous air pollutants (HAPs) from phase II vapor recovery systems with combustion processors at gasoline stations. The select HAPs of interest include benzene, 1,3 butadiene, and aldehydes (carbonyls). Ethyl benzene, toluene, and xylenes may be included.

According to a Material Safety Data Sheet (MSDS), gasoline contains benzene (<5%), toluene (<6.5%), ethyl benzene (<1.4%), and xylene (<7.7%). Benzene and 1,3 butadiene may be emitted from these combustion processors as products of incomplete combustion (PICs). The processors to be tested have been certified by the ARB, but only with respect to the control of total hydrocarbons.

1.2 Test Summary

A gasoline station with either a Hirt or Hasstech Phase II vapor recovery system will be selected for testing. Stack parameters (including total hydrocarbons (THC), carbon dioxide (CO_2), CO, and NOx) and inlet parameters (including inlet total hydrocarbons and volume) will be measured in accordance with U. S. Environmental Protection Agency (US EPA) Method 2A or California Air Resources Board (CARB) Test Procedure TP-201.2 for stack flows. Benzene and 1,3 butadiene samples will be collected from the stack of the vapor recovery combustion processor in Tedlar® bags in accordance with CARB Method 422 for analysis by ARB Method 1002. Aldehyde samples will be collected in DNPH-impregnated cartridges or DNPH impinger solution for CARB Method 1004 analysis. Background samples and sample blanks and spikes will be prepared and analyzed with the grab samples. Grab samples will be returned to ARB laboratories within 72 hours of sample collection for analysis for benzene, 1,3-butadiene, and aldehydes (carbonyls).

2.0 SOURCE DESCRIPTION

Hasstech and Hirt combustion processors are similar in how they destroy gasoline fumes. Excess gasoline fumes are piped to a combustion processor at the gasoline station. An igniter ignites the gasoline fumes when they reach a combustible concentration. Combustion air is brought into the processor to complete the destruction of gasoline vapors.

For sampling purposes, stacks for both units have similarities. Both are relatively low flow, usually have no sampling ports, and are capped with a flame arrester and/or weather cap. These features make normal stack flow measuring methods (ARB and US EPA Methods 1 through 4) and isokinetic sampling methods impossible. (Gaseous sampling such as grab samples for benzene, 1,3 butadiene, and aldehydes does not require isokinetic sampling.)

3.0 SAMPLING LOCATIONS

Hasstech systems usually have a rectangular stack and Hirt systems usually have a round stack. Hirt engineers have indicated their stack may also be too short for sample collection and may require a stack extension. Design of an adequate Hirt stack extension with sampling location is complicated by the Hirt stack design, which requires flow around the cap instead of straight out the stack. Hasstech stacks do not appear to need a stack extension.

The presence of caps on the stacks of both systems eliminates the need for stack velocity for modeling purposes. Buoyancy, for modeling purposes, is based on exhaust gas temperature at the stack exit. Volume flow is required and will be calculated from measured inlet flow and gaseous measurement of inlet and exhaust hydrocarbon concentrations, and exhausted carbon dioxide and carbon monoxide concentrations.

The stack caps will require traversing the stack with the carbon monoxide and carbon dioxide monitors to determine a location for average stack gas concentrations. That will be the location for collecting gaseous grab samples.

4.0 SAMPLING METHODS

Sampling and analysis will be in accordance with ARB proposed vapor recovery test procedure TP-201.2H, “Determination of Hazardous Air Pollutants from Vapor Recovery Processors.” Proposed TP-201.2H is a compilation of sampling and analytical methods approved by the ARB or promulgated by the US EPA.

4.1 Flow Determination

Stack volume flow will be determined in accordance with US EPA Method 2B, “Determination of Exhaust Gas Volume Flow Rate from Gasoline Vapor Incinerators,” as specified in proposed TP-201.2H.

Volume flow rate (by volume meter) and inlet total hydrocarbon concentration (by CEM) are measured at the incinerator inlet. Carbon dioxide, carbon monoxide, and exhaust total hydrocarbons (by CEMs) are measured at the incinerator exhaust stack, or stack extension, if required. Inlet volume is multiplied by the ratio of total carbon at the inlet and outlet in accordance with US EPA Method 2B to calculate total exhaust flow. The method assumes no auxiliary fuel.

Oxides of nitrogen (NOx) will be monitored with the other exhaust gases. NOx is not needed for flow determination, but is a requirement for proposed CP-201.

4.2 Benzene and 1,3 Butadiene

Stack concentrations of benzene, 1,3 butadiene and, possibly, toluene, ethyl benzene, and xylene will be collected in Tedlar bags. Prior to testing, the Tedlar bags will be inflated with 99.9% pure (or purer) nitrogen, leaked checked over 24 hours, and checked for contamination.

Bag samples will be collected in accordance with CARB Test Method 422, "Determination of Volatile Organic Compounds in Emissions from Stationary Sources," as specified in proposed TP-201.2H, "Determination of Hazardous Air Pollutants from Vapor Recovery Processors." A Teflon-lined stainless steel sample probe with less than 10 feet of Teflon sampling line will be inserted in the stack or stack extension to the proper sampling location as determined by the exhaust CEMs. The sampling line will be connected to a Tedlar bag in a rigid box. The rigid box will be evacuated to inflate the bag with stack gas.

Bag sampling will start after the incinerator blower has started and stack temperature starts to rise. Sampling will stop when the blower stops. Sampling with the same bag will continue this way until the bag is 50 to 80 percent full. Only full "burns" will be sampled and at a rate of one or more "burns" per sample. Sampling rate will depend on sample bag volume and will be at least 1 lpm. Sample bags will be 10 liters or larger.

4.3 Aldehydes (Carbonyls)

Stack concentrations of aldehydes (formaldehyde, acetaldehyde, etc.) will be collected with impingers containing an aqueous acidic solution 2,4-dinitrophenyl-hydrazine (DPNH) or DPNH-impregnated cartridges. The impinger method will require a chemist on-site to prepare the solution to reduce contamination. Common source test materials like acetone, inks, and adhesives are contamination sources. The cartridge method will not require an on-site chemist to reduce contamination. But the cartridge method will require two or more cartridges in series to prevent stack gas interference and "sample breakthrough."

Samples will be collected in accordance with ARB Test Method 430, "Determination of Formaldehyde and Acetaldehyde in Emissions from Stationary Sources," as specified in proposed TP-201.2H. A Teflon-lined stainless steel sample probe with less than 10 feet of Teflon sampling line will be inserted in the stack or stack extension to the proper sampling location as determined by the exhaust CEMs. The sampling line will be connected to the DPNH cartridge or impingers. The sample will be pulled into the DPNH by a flow controllable pump with a volume meter.

Sampling will start after the incinerator blower has started and stack temperature starts to rise. Sampling will stop when the blower stops. Only full "burns" will be sampled and

at a rate of one or more “burns” per sample. Sampling rate will up to 1.5 lpm for about 20 minutes for cartridges or 0.1 to 0.5 lpm for up to an hour for impingers.

5.0 SAMPLING EQUIPMENT

(Use of trade or manufacturer’s names are not a recommendation nor endorsement by the ARB.)

5.1 Flow Measurement

5.1.1 Volume Meter, Manometer, Temperature Monitor, Barometer, and Stopwatch. A Roots volume meter and supporting equipment meeting the specifications of US EPA Method 2A or CARB Test Procedure TP-201.2 (same specifications) will be used for inlet volume flow. A stopwatch is necessary for converting volume to flow rate (from cubic feet to cubic feet per minute). Manometer, temperature monitor, and barometer are needed to convert flow to standard conditions (from cubic feet to standard cubic feet).

5.1.2 Hydrocarbon Analyzers (2). Two hydrocarbon analyzers and supporting equipment described in US EPA Test Method 25A (FID analyzer) and 25B (NDIR) or CARB Test Procedure TP-201.2 (same specifications) will be used. An NDIR HC analyzer will be used for inlet measurements. An FID HC analyzer is recommended for exhaust measurements.

5.1.3 CO Analyzer. A CO analyzer and supporting equipment described in CARB Test Procedure TP-201.2 or CARB Test Method 100 (same specifications) will be used.

5.1.4 CO_2 Analyzer. A CO_2 analyzer and supporting equipment described in CARB Test Procedure TP-201.2 or CARB Test Method 100 (same specifications) will be used.

5.1.5 NOx Analyzer. A NO_x analyzer and supporting equipment described in CARB Test Method 100 will be used.

5.2 Benzene and 1,3 Butadiene Sampling

5.2.1 Tedlar® Sampling Bags. Tedlar® sampling bags meeting or exceeding specifications in CARB Test Method 422 will be used. At least three (3) sample bags for stack samples plus one (1) bag for ambient sample will be collected. Additional bags will be used as required by ARB Method 422, 1002, and 1003 for blanks and spikes. Bags are to be leak-checked, purged, cleaned, and contamination checked by the analytical laboratory prior to going into the field.

5.2.2 Sample Probe. Use Teflon®-lined stainless steel tubing to draw the sample from the stack. Teflon® should not be used in locations above 750^{o} F. Probe should be long enough to traverse stack and at the same time avoid injury to the probe handler.

5.2.3 Sample Line. The sample line is made of Teflon® and should be as short as possible but no longer than 10 feet. The sample line will have adapters at each end for leak-tight connections to the sample probe and Tedlar bags. (Sample lines longer than 10 feet must be insulated and heated to 225 – 275 degrees Fahrenheit during sample collection).

5.2.4 Vacuum Pump. A vacuum pump and sufficient supporting equipment per CARB Test Method 422 will be used to purge the sample line and probe prior to collecting samples and evacuate the bag sampler for sample collection.

5.2.5 Bag Sampler. A rigid container bag sampler and supporting equipment described in CARB Test Method 422 will be used. Only sample probe, line and bag assembly must be leak-tight.

5.2.6 pH Indicator. A pH indicator will be used to indicate if stack gas pH is 4 or higher in accordance with CARB Test method 422.

5.3 Aldehydes

Use sampling and support equipment described in CARB Test Method 430.

5.3.1 DPNH Cartridges (Commercially available). At least three (3) samples for stack samples plus one (1) ambient sample will be collected. A sample will consist of at least 2 cartridges in series. Cartridges will be wrapped to protect from light from the start of sample collection to sample recovery. Additional cartridges will be used as required by ARB Test Method 430 and Method 1004 for blanks and spikes.

5.3.2 Sample Probe. Teflon®-lined stainless steel tubing will be used to draw the sample from the stack. Teflon® can not be used in locations above 750^{o} F. A 3 to 4 foot long probe should be long enough to traverse stack.

5.3.3 Sample Line. Ten (10) feet or less of ¼ inch or smaller Teflon® sampling line will be used. Only new unused tubing will be used prior to the start of testing. The sample line will have Teflon®-lined adapters as needed for leak-tight connections to the sample probe and DPNH cartridges. (Sample lines longer than 10 feet must be insulated and heated to 225 – 275 degrees Fahrenheit during sample collection).

5.3.4 Vacuum Pump. A vacuum pump with at least five (5) liters per minute (lpm) capacity and on/off capability will be used per CARB Test Method 430 for sample collection.

5.3.5 Rotameter. A flow controllable rotameter accurate at 1.5 lpm will be used.

5.3.6 Volume Meter. A volume meter capable of measuring up to 100 liters in 0.1-liter increments will be used.

6.0 TEST PROGRAM

The objective of this test program is to determine concentrations of HAPs such as benzene, 1,3 butadiene, and aldehydes from phase II vapor recovery systems with combustion processors at gasoline stations. While collecting samples for HAPS , ARB staff will collect information to determine flow from the combustion processor, and will monitor gasoline throughput at the gasoline station.

6.1 Pre-Test

6.1.1 Choose a gasoline station in compliance with pressure decay (TP-201.3) and air/liquid ratios (TP-201.5) requirements.

6.1.2 Determine location of inlet and outlet sampling and monitoring locations in accordance with US EPA Method 2B or CARB Method TP-201.2. Check stack temperature during a burn cycle at the outlet sampling location. Temperatures above 750^{o} F may indicate sampling location is too near the combustion zone. Relocate outlet sampling location or use a stack extension if necessary.

6.1.3 Assemble, install, and leak check flow monitoring equipment (including analyzers sampling system) in accordance with US EPA Method 2B or CARB Test Procedure TP-201.2 and NOx analyzers in accordance with CARB Test Method 100.

6.1.4 Assemble the bag sampling system in accordance with CARB Test Method 422. During one or more of the observed burns, purge the sampling line and probe with stack gases using the vacuum pump. Purge the sampling probe and lines with a volume of stack gas equal to at least three (3) volumes of the sample line and probe. Leak check sampling probe, line, and sample bag. (If NOx is greater than 5 ppm and stack gas acidity is pH 4 or lower, 1,3 butadiene spikes must be added to the grab sample.)

6.1.5 Assemble the aldehydes sampling system in accordance with CARB Test Method 430.

6.1.6 Product dispensing (vehicle fueling) may occur during sampling. No samples for HAPS (aldehydes, 1,3 butadiene, and benzene) will be collected within three hours after a Phase I delivery.

6.2 Test

Check stack temperature, set up flow equipment, and confirm monitoring equipment is operating correctly during one or more observed burns.

Collect at least three grab samples each for benzene and 1,3 butadiene samples and aldehydes samples.

6.2.1 Prior to sample burn, operate flow monitoring equipment, including CO, CO2, and THC analyzers, in accordance with US EPA Method 2B or CARB Test Procedure TP-201.2.

6.2.2 Operate NOx analyzer with the analyzers mentioned above in accordance with CARB Test Method 100.

6.2.3 Traverse the stack with the continuous emission monitors (CEM) sampling probe. Use the CEM results to locate CEM, aldehydes, benzene, and 1,3 butadiene sampling locations based on average stack concentrations of the measured stack gases.

6.2.4 Inspect the Tedlar® bags. Remove excess gas from bags. Connect Tedlar® bag to the sample line. Complete any initial label recordings.

6.2.5 Record initial readings of volume meter, gasoline dispensing totalizer(s) and mark analyzer strip charts and/or dataloggers in a manner consistent with TP-201.2 prior to sample collection.

6.2.6 Insert 1,3 butadiene and benzene sampling probe(s) into the stack and begin evacuating the rigid bag sampling container. At the start of the next burn (indicated by rising stack temperature), open the flow control valve and collect the sample.

6.2.6.1 If the burn stops before the sample is collected, close the flow control valve immediately at the end of the burn. Reopen the valve at the start of the next burn. Continue opening and closing the valve with the burn cycles until the sample(s) is collected.

6.2.6.2 After the Tedlar bag is full enough, close the flow control valve and sample bag valve.

6.2.6.3 Disconnect the bag sample from the sampling line. Complete the sample label. Transfer required information to the chain of custody log.

6.2.7 Insert aldehydes sampling probe into the stack and collect the sample in a manner consistent with bag sampling above. To the extent practicable aldehyde samples may be collected in parallel with bag samples

6.2.8 After sample collection, mark strip charts and record final meter and totalizer readings for the collected sample in a manner consistent with TP-201.2 and CARB Test Method 100.

6.2.9 Repeat the grab sampling cycle for the second, third, and any additional aldehydes, 1,3 butadiene, or benzene samples. Do not collect samples at a rate greater than one aldehydes, 1,3 butadiene, and benzene sample per burn. If necessary, more than one bag or cartridge set will be used for a complete sample.

6.2.10 Immediately after collecting a set of stack samples for aldehydes, 1,3 butadiene, and benzene, collect ambient air samples for aldehydes, 1,3 butadiene, and benzene. If direct sampling and analysis is used for 1,3 butadiene, the same set up should be used to analyze ambient air. The ambient sample is used to determine background concentrations of the target compounds.

6.2.10.1 Select an ambient air location near the processor but upwind of it, the gasoline dispensers, and other possible gasoline vapor vents.

6.2.10.2 Holding the probe straight up in the air with the sampling end 8 feet or higher above ground.

6.2.10.3 Purge the sample line in a manner consistent with the purge for the stack samples. Purge volume should be near the same as purge volume for the stack samples.

6.2.10.4 Connect the ambient sample Tedlar bag, Summa-polished canister, or aldehydes sample train to the sample line as appropriate for the ambient sample to be collected. Connect the direct sampling and analysis system if this method is used to determine 1,3 butadiene stack gas concentrations.

6.2.10.5 With the probe still in the air, open the sample flow control valve.

6.2.10.6 When the sample is collected, close the valve and disconnect from the sample line.

6.2.10.7 If another stack sample is to be collected after the ambient sample, purge the sample probe and sample line with stack gas as required above.

6.3 Post-Sampling Procedures

Protect bag and cartridge samples from light. Transport samples in accordance with CARB Test Method 422 or 430 as appropriate for analysis as soon as possible. Analyze grab samples within 72 hours of collection.

7.0 QUALITY ASSURANCE

7.1 Flow Determination

In accordance with ARB Test Method 100, equipment and monitors (volume meter, continuous emissions, temperature and pressure monitors) used to collect data for flow rate determinations have current multipoint calibrations. On-site, continuous emission monitors will be calibrated against zero, mid-point, and span gases at the beginning and end of the test. Additionally, system bias checks with zero and mid-point or span gas will also be performed at the start and end of the test.

7.2 Benzene and 1,3 Butadiene

All Sample bags will be made from virgin (unused) Tedlar material. The bags will be purged 5 times with pure (>99.99%) nitrogen to eliminate contaminates. The last purge will remain in the bags for at least 24 hours to leak-check the bags. The last purge will then be analyzed by GC/MS to determine any contaminate level.

A field blank will be collected by forcing nitrogen through the bag sampling probe and sample line into an empty Tedlar bag.

A 1,3 butadiene matrix spike should be added to a sample bag to determine 1,3 butadiene degradation.

All bag samples will be collected and stored in opaque containers. A “Chain of Custody” form will accompany each bag sample. The bags must be analyzed within 72 hours of sample collection.

7.3 Aldehydes

All sampling train components that may contact the flue gas during sampling are made of glass or Teflon.

A blank train will be collected with each aldehydes sample train. Blank trains are assembled, leak checked, recovered, and analyzed with the sampling train they are paired to. After performing the initial leak check, the blank train is sealed and left in the test area for the duration of the sampling period.

A “Chain of Custody” form will accompany each aldehyde sample including blanks.